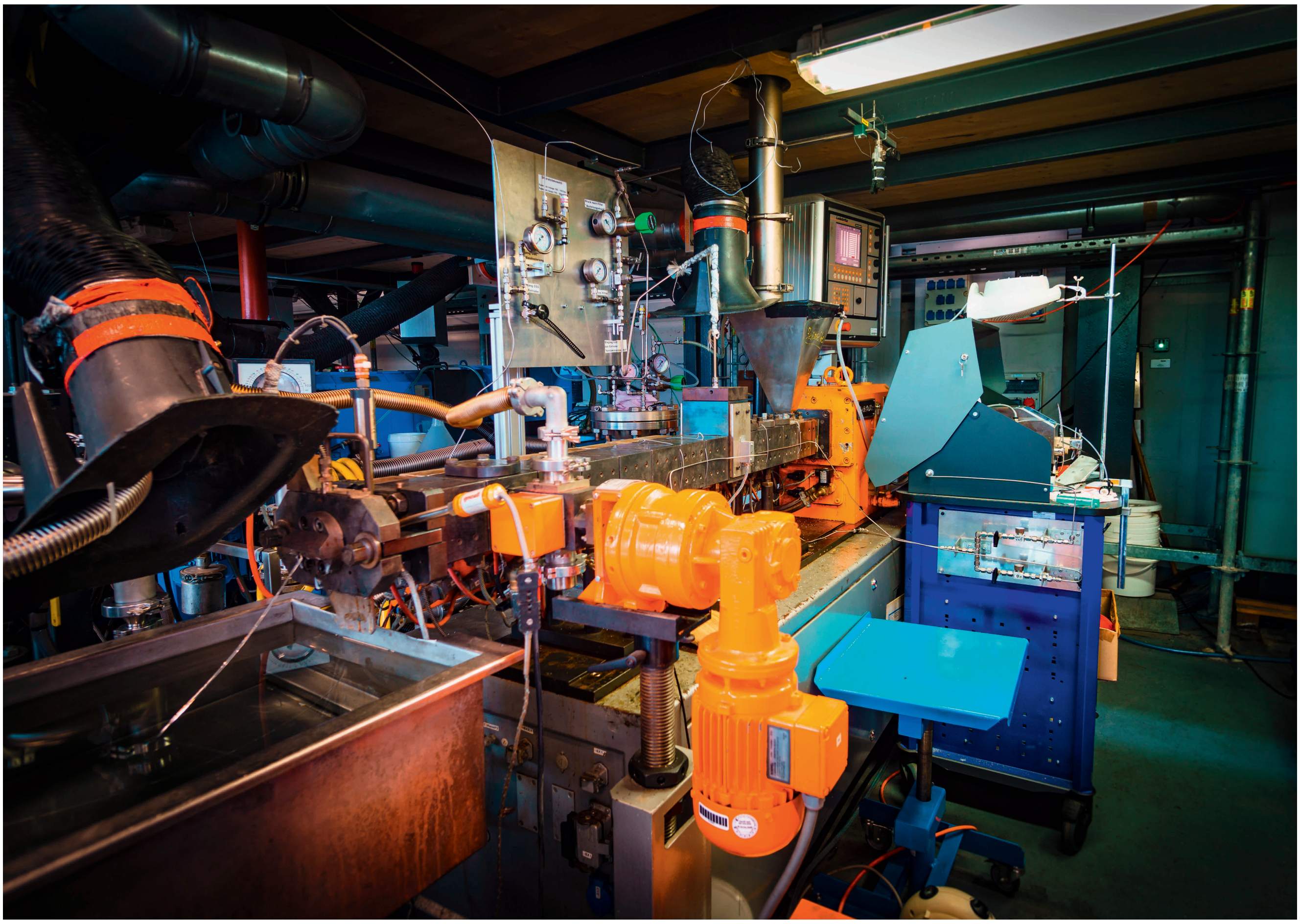
Providing Recyclates with Reduced Emissions

Physical Recycling of Plastics

Besides chemical recycling technologies, continuous physical material recycling processes offer advanced, economically attractive alternatives for melt purification. Fraunhofer ICT has analyzed stripping agent-assisted and extractive extrusion processes.



Pilot plant for extractive extrusion at Fraunhofer ICT in Pfinztal, Germany. © Fraunhofer ICT

Stricter regulative framefork on environmental and health impact require minimum recyclate contents, reduction of CO_2 emissions, or the consumer demand for high-quality products from recyclates have led to an increased industry focus on emissions and material purity. Besides chemical recycling technologies, improved continuous physical material recycling processes offer advanced and economical alternatives for melt purification and make it possible to provide recyclates with reduced emissions and contamination.

Fraunhofer ICT has two different continuous technologies available: stripping agent assisted extrusion (stripping) and extractive extrusion. Both processes make use of fluids tailored to the particular separation task during extrusion to improve the cleaning performance. Stripping focuses on the removal of odorous substances and/or of byproducts from preprocessing such as printing inks or adhesion promoters. In contrast to stripping, extractive extrusion is also suitable for the decontamination of undesirable substances that are no longer compliant by regulation. The two methods differ according to the technical effort required to adapt them to an existing twin-screw extruder. Since the stripping agent assisted process can be much more easily integrated compared to the extractive extrusion process, this method should generally be preferred, if the physical material parameters consider it feasible.

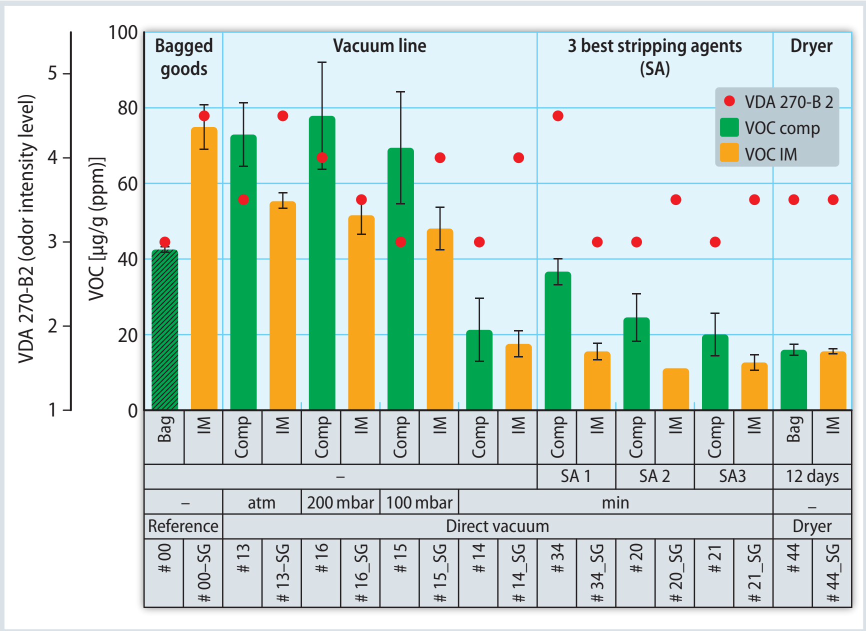


Fig. 1. Characteristic values for the VOC emissions and odor after treatment in the stripping process (Comp = after extrusion, IM = after injection molding, SA = stripping agent). Source: Fraunhofer ICT; graphic: © Hanser

In stripping, the polymer is fed into the extruder via the main hopper. After the melting zone, a melt sealing via a compression must be provided to prevent backflow of the stripping agent. The stripping agent is subsequently mixed into the polymer. In the degassing zone, the stripping agent, with the dissolved, undesirable components, is vacuum degassed and the purified polymer is finally discharged through the nozzle. The key advantage of this method is that, assumed that the plant is correctly configured, only a little shear energy is introduced, and the material is thereby processed with low stress.

Stripping: a Stripping Agent Removes Undesirable Components

For stripping, a wide variety of stripping agents can be chosen depending on the task. Common stripping agents are for example water (H_2O), nitrogen (N_2) and carbon dioxide (CO_2), as well as alcohols. CO_2 has proven to be an effective stripping agent as it dissolves very well in polymers and thereby improves the removal of the volatile substances in »

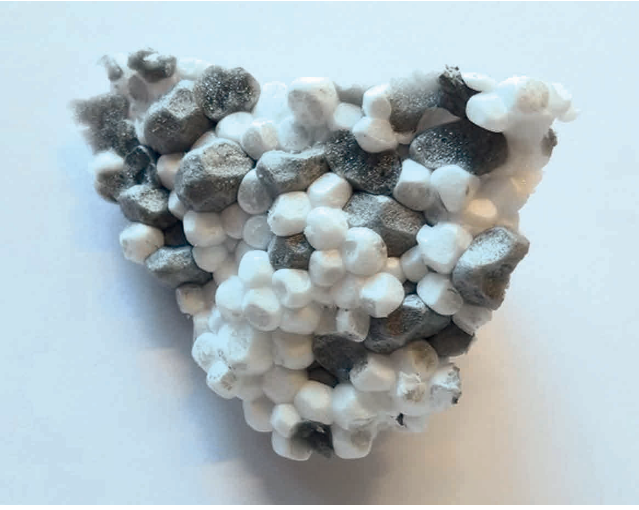


Fig. 2. Starting material EPS. © Centexbel

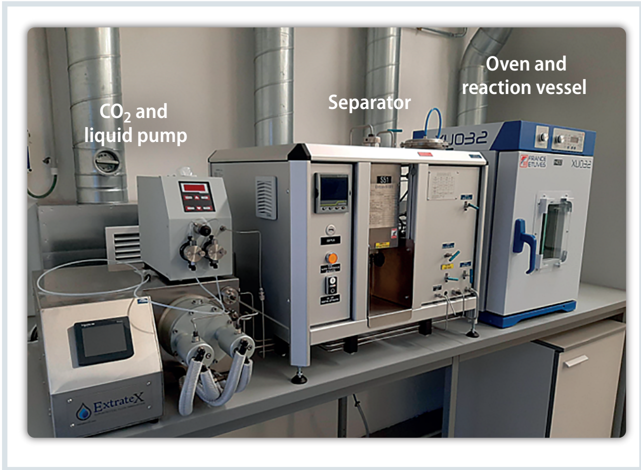


Fig. 3. The reactor at Centexbel with liquid pump, reaction chamber in the oven and a separator for separating the contamination. © Centexbel

Info

Text

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the degassing step. The common factor of all stripping agents is that, because of the viscosity reduction of the polymer, their addition leads to a continuous renewal of the melt surface and thus to a considerable improvement of the degassing performance in the extruder.

The cleaning performance can be controlled by means of the used proportion of the stripping agent to the polymer. Analysis of the emissions is usually performed according to VDA 277 (headspace GC) or VDA 278 (thermal desorption analysis). Both standards record the concentration of volatile organic compounds (VOCs) and evaluate them using suitable test parameters. In contrast to emissions, the odor reduction, on the other hand, can only be subjectively recorded, since every individual perceives the odor differently. The olfactory impression of a product also only rarely correlates with the data from the emission analysis and can thus only be registered to a limited extent. The success of an odor reduction is therefore evaluated by a test panel (odor test acc. to VDA 270). Alternatively, the first tests at Fraunhofer ICT according to the new standard ISO 16000–28 also indicated its feasibility to plastic pellets. With this method, a specially trained odor panel and the use of comparison standards lead to reproducible results.

The extraction process is analogous to the stripping process up to the first sealing zone. The supercritical CO_2 is metered into the extruder after the sealing zone and is incorporated in the extraction zone parallel to the melt in the free space between the screw, barrel and melt. In the process, some of the CO_2 dissolves in the melt. At the end of the extraction zone, the supercritical CO_2, together with the contaminants dissolved in the CO_2, is removed from the melt again.

Somewhat More Complicated: Extraction

After discharge into a flash tank (phase separator), the pressure of the supercritical CO_2 is finally reduced. Because of the pressure drop, the solubility in CO_2 decreases and the dissolved contaminants are precipitated out. Depending on the profitability and the set CO_2 throughput, a reclamation unit for the stripping agent can be used. The extraction process generally uses CO_2 in the supercritical state. But other liquids such as water or alcohols are also possible. In a similar way to the stripping process, the extraction performance can be controlled via the amount of supercritical CO_2 used, as well as via the amount of an additional contaminant-specific solvent.

In a study, the potential of the stripping process to remove odor-intensive components and volatile organic compounds (VOCs) from recycled polypropylene was investigated. For this, seven stripping agents H_2O, CO_2, N_2, ethanol, isopropanol and two commercial additives were used. For comparison, a reference sample was treated in parallel in a pellet dryer for two weeks to simulate silo degassing. Determination of the VOC emissions and odor notes were performed on pellets and subsequently tensile test bars were produced from them by injection molding.

The evaluation (**Fig. 1**) shows very good results regarding the odor and emission reduction using the stripping process, on both the pellets and the injection-molded panels. Based on the bag reference sample, the emissions after extrusion and injection molding increased significantly. A reduction can only be observed when vacuum is applied and it increases with higher vacuum intensity. High absolute vacuum pressures as well as exclusively atmospheric degassing are practically ineffective. Furthermore, the results show that low absolute vacuum pressures are necessary to obtain low emissions (#14), but lead to unchanged high odor notes. Only the additional introduction of stripping agents promotes a further reduction of the odor values. For the investigated polypropylene, H_2O and CO_2 proved to be the most effective stripping agents for emission and odor, see **Figure 1**. The results of degassing in the pellet dryer show good results for VOC and odor; however, they are time consuming and comparatively energetically unfavorable. Fraunhofer ICT coordinates the Europe-sponsored CREAToR project for eliminating today forbidden legacy additives from polymers, so that they can be used again as recyclates.

Reprocessing Waste Streams Contaminated with Illegal Substances

In CREAToR, hazardous and already forbidden brominated flame retardants are eliminated from waste streams such as polystyrene (PS) foam (**Fig. 2**), using extractive extrusion. The purified polymers are turned back into new high-quality applications, for example in the construction sector, automotive sector and the aeronautic sector.

The first experiments were conducted for insulation panels from the building and construction sector on a batch scale to investigate the extraction efficiency of different solvents under different conditions (temperature, pressure). Then the parameters were transferred to continuous processing. As the project continued, two pilot lines were set up for the extraction, based on the use of environmentally friendly extraction solvents, namely deep eutectic solvents and supercritical CO_2. The pilot plant at the Centexbel institute is suitable for performing extraction at up to 150 °C and 700 bar in batch (**Fig. 3**). The continuous extractive extrusion line at Fraunhofer ICT is able to treat polymer streams at up to 10 kg/h with a CO_2 volume stream of 300 g/h at pressures over 120 bar and temperatures over 160 °C (**Title figure**). The first results from the extraction trials show promising results. ■